Increasing the Oxidative Stability of Poly(Dicyclopentadiene) Aerogels by Hydrogenation

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Increasing the oxidative stability of poly(dicyclopentadiene) aerogels by hydrogenation

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Poly(dicyclopentadiene), Aerogel

ABSTRACT: Ring opening metathesis polymerization (ROMP) of cycloolefins is a promising new route for the preparation of polymeric aerogels. The resulting unsaturation in the polymer backbone, however, makes these particular systems susceptible to oxidative degradation under ambient conditions. One method to increase the oxidative stability of these aerogels is to hydrogenate the material. In the present study, hydrogenation of poly(dicyclopentadiene) gels was achieved through thermolysis of *para*-toluenesulfonyl hydrazide in the presence of tripropylamine followed by solvent exchange and supercritical drying to form the hydrogenated aerogel (H-*p*DCPD). Aerogels were prepared with varying densities and were characterized by FTIR-ATR, elemental analysis, BET, SEM, XPS, DSC and TGA. The oxidative stability of H-*p*DCPD aerogels over *p*DCPD was investigated through thermolysis in the presence of atmospheric oxygen. We report herein the synthesis and characterization of this new material.

There is increasing interest in the study of aerogels, a class of materials exhibiting low density, high porosity, high surface area and low thermal conductivity.[1-5] Aerogels are typically synthesized by taking a wet gel precursor and subjecting the material to supercritical drying, this process negates the effects of capillary stresses that otherwise lead to gel destruction or shrinkage upon solvent removal. The result is a solid network wherein the liquid has been replaced with the ambient atmosphere, giving a low-density scaffold. Depending on their chemical composition, aerogels have found some applications as thermal[6] and acoustic insulators[7], supercapacitors[8], and potential chemical/energy storage platforms[9]. The uses of aerogels are as varied as their composition; the first aerogels being composed of silica[10] followed soon after by the preparation of both transition metal[11] and lanthanide oxides[12]. Though 'classic' aerogels are oxide-based; researchers have begun to successfully prepare organic aerogels such as resorcinol-formaldehyde[1], cellulose[13], polyurethane[14], and, of interest to us, poly(dicyclopentadiene)[15].

Materials based on the polymerization of dicyclopentadiene (DCPD) to poly(dicyclopentadiene) (*p*DCPD) are gaining interest likely due to the ease of synthesis, cheap material cost, tolerance of polymerization conditions to oxygen and water, and the potential for polymer modification through the reaction of *p*DCPD alkenes along the polymer backbone[16]. A combination of additional physical characteristics such as good physical and electrical properties have provided the impetus for its' use as a replacement material for reaction injection molding parts[17]. The popularity of *p*DCPD and continued interest in aerogels has naturally led to the recent preparation *p*DCPD aerogels[15].
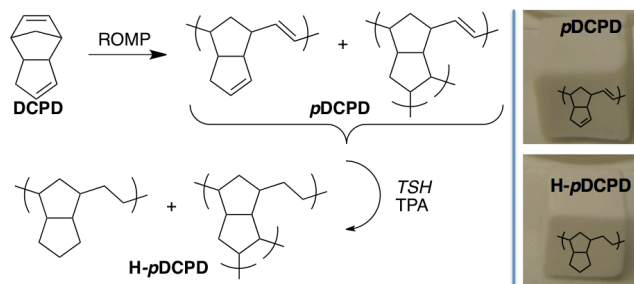

Figure 1. The preparation of *poly*(dicyclopentadiene) (*p*DCPD) gels through ring opening metathesis polymerization (ROMP). Hydrogenation of the gel using *para*-toluenesulfonyl hydrazide (*TSH*) in the presence of tripropylamine (TPA) results in formation of hydrogenated *poly*(dicyclopentadiene) (H-*p*DCPD). Supercritical drying leads to aerogels, shown to the right.

These *p*DCPD aerogels are easily prepared first by ROMP of DCPD then supercritical CO_2 drying of wet gels to give aerogels with nominal densities ranging from ca. 30 to 300 mg mL^{-1}. The aerogels are typically fibrous in nature with large surface areas (> 200 m^2 g^{-1}) and low thermal conductivity (ca. 20 mW m^{-1} K^{-1}) creating the possibility of its use as a novel insulation material.

The drawback of *p*DCPD materials is that the high density of alkenes along the polymer backbone makes this material susceptible to oxidative damage.[18] In many cases, the preparation of *p*DCPD polymers is coincident with the formation of small amounts of oxidation products along the polymer. In the case of solid *p*DCPD films, the oxidation process forms an oxide film that prevents further oxidation of the inner material[19]; this is likely not the case for an aerogel wherein the material porosity is larger than 90 % and an outer, oxide film will not

inhibit oxidation of the inner domains. To protect these aerogels from oxidative stress, we report herein that the hydrogenation of *pDCPD* gels followed by supercritical drying to form hydrogenated H-*pDCPD* aerogels is a viable route to such an oxidatively stable aerogel material.
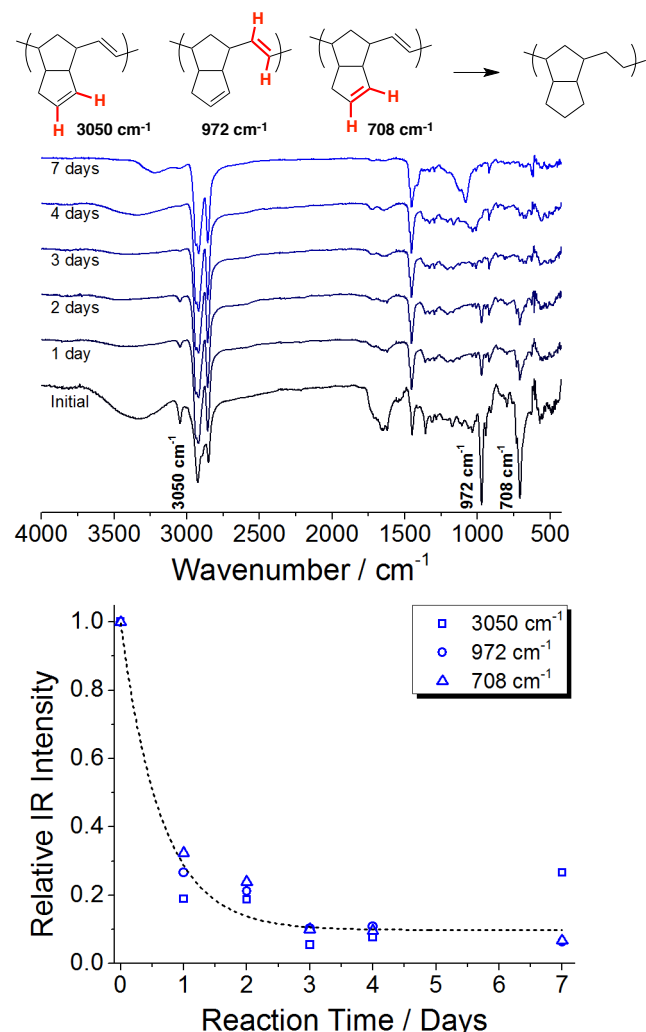

Figure 2. Hydrogenation of *pDCPD* gels was monitored by FTIR-ATR, monitoring resonances at 3050 cm^{-1}, 972 cm^{-1} and 708 cm^{-1}. Above, hydrogenation was conducted at 75 °C in the presence of 8 eq. *TSH* and 32 eq. TPA in 1,2-dichlorobenzene on 30 mg mL^{-1} *pDCPD* gels for the annotated number of days. Attributed resonances are noted above the IR spectra. A plot of the relative IR intensity (bottom) versus reaction time shows consumption of the IR resonances after ca. 3 days of reaction. Fit provided to guide the eye.

To hydrogenate *pDCPD* gels to H-*pDCPD*, we used *para*-toluenesulfonyl hydrazide (*TSH*), a well-established hydrogenation agent that has found wide utility in polymer hydrogenation reactions[20]. For example, polyethylene can be prepared by hydrogenation of polybutadiene[21], or further block copolymers of hydrogenated norbornene-*b*-polyethylene are also generated in this way[22]. At elevated temperatures, *TSH* decomposes to form diimide and *para*-toluenesulfinic acid; in the presence of alkenes the diimide adds two hydrogen atoms across the double bond and nitrogen gas is released. Since we conducted hydrogenation reactions on solid *pDCPD* gels, we found that the reaction required both longer reactions times and lower temperatures to (1) decrease the rate of N$_2$ gas evo-

lution that leads to trapped bubbles in the *pDCPD* gel and/or degradation of the material and (2) allow the hydrazide to percolate the gel network to achieve full hydrogenation. Additionally, the use of tripropylamine was required to inhibit the reaction of *pDCPD* alkenes with the formed sulfinic acid[20].

We first determined the reaction temperature and duration required for hydrogenation of the *pDCPD* gels. 30 mg mL^{-1} *pDCPD* gels [30-*pDCPD*] were subjected to hydrogenation for varying times in the presence of 8 equivalents *TSH* and 32 eq. TPA at 75 °C for up to 7 days of reaction in 1,2-dichlorobenzene. The extent of reaction was followed using FTIR-ATR on supercritically dried aerogels by monitoring the intensity of IR absorbances at 3050 cm^{-1} (sp^2 =C-H), 972 cm^{-1} (*trans* double bond, *pDCPD* main chain) and 708 cm^{-1} (*cis* cyclic double bond, *pDCPD* unopened cyclopentene).[23] An analysis of the relative IR intensity of hydrogenated H-*pDCPD* aerogels (Figure 2) showed consumption of alkene absorbance in the IR spectra after ca. 3 days of reaction under these conditions, forming hydrogenated 30-H-*pDCPD*.

The effect of *TSH* was next investigated, 30-*pDCPD* gels (30 mg mL^{-1}) were hydrogenated for 3 days at 75 °C wherein the number of equivalents (versus alkenes) of *TSH* was increased from 1 eq. to 10 eq. An analysis of the relative IR intensities of supercritically dried aerogels versus *TSH* showed a complete reaction when greater than 6 eq. of *TSH* was used in the reaction (see SI, Figure S1).
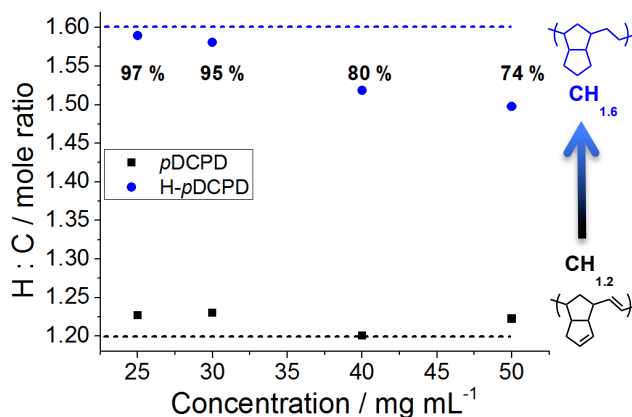

Figure 3. Elemental analysis of *pDCPD* and H-*pDCPD* aerogels of varying initial densities (as mixed, not directly measured here), here 100 % hydrogenation leads to a CH$_{1.6}$ material. The percentages indicate the degree of hydrogenation as calculated from the CH$_x$ balance.

To verify the formation of H-*pDCPD* aerogels, we next hydrogenated a series of *pDCPD* gels of varying initial density under our 'standard condition' (75 °C, 8 eq. *TSH*, 32 eq. TPA in 1,2-dichlorobenzene) and the atomic compositions were determined by elemental analysis (Figure 3). The extent of hydrogenation decreased with initial *pDCPD* concentration, from 97 % hydrogenation (25-H-*pDCPD*) to 74 % hydrogenation (50-H-*pDCPD*). This concentration effect is likely the result of the amount of DCPD incorporated into the *pDCPD* gel prior to hydrogenation. For example, a series of *pDCPD* gels were prepared in 1cm^3 glass molds, supercritically dried and weighed. The percent incorporation of DCPD into these gels was found to increase with increasing mixed density. A 25-*pDCPD* aerogel was found to contain only ca. 12 mg material, or 48 % DCPD incorporation into the gel followed by 67 %, 75 % and 80 % for 30-, 40- and 50-*pDCPD* aerogels re-

spectively. The actual amount of DCPD in the pDCPD gels prior to hydrogenation shows that the actual *TSH* content per alkene used in the hydrogenation reaction is largest at lower concentration (ca. 25-pDCPD, 12 mg DCPD; actual *TSH* = 16 eq.) versus high-density pDCPD precursors. A plot of the actual *TSH* equivalents versus the hydrogenation efficiencies (see SI, Figures S2) obtained from elemental analysis indicates that > 12 equivalents of *TSH* are required to obtain > 95 % H-pDCPD aerogels under these reaction conditions.

The processing of wet gels into aerogels is commonly followed by shrinkage of the wet gel to an aerogel of increased density.[24] We therefore monitored the densities of pDCPD and H-pDCPD aerogels, and, in addition, the morphological characteristics of the as-formed aerogels. The pDCPD gels were first prepared in either cylindrical or square molds, then supercritically dried (SCD) with CO_2. After SCD, the samples were weighed and measured to determine the aerogel density (Table 1). The resulting pDCPD aerogels had densities ranging from 30 mg mL^{-1} (25-pDCPD) to 109 mg mL^{-1} (50-pDCPD), or shrinkage factors (final density ÷ initial density) that increased from 1.2 to 2.2. By comparison, the densities of H-pDCPD aerogels ranged from 48 mg mL^{-1} (25-H-pDCPD) to 166 mg mL^{-1} (50-H-pDCPD), or shrinkage factors from 1.9 to 3.3.

Table 1. Measured densities (*d*), pore volume (PV), pore diameter (PD) and aerogel surface area (SA) for pDCPD and H-pDCPD aerogels. Numbers beneath Sample ID indicate the mixed density (mg mL^{-1}) of the wet gel prior to hydrogenation and supercritical drying.

Sample ID	*d* / mg mL^{-1}	PV / mL g^{-1}	PD / nm	SA / m^2 g^{-1}
25-pDCPD	30	0.87	13.9	303
H-pDCPD	48	0.79	25.5	192
30-pDCPD	42	1.02	15.8	303
H-pDCPD	71	0.93	18.5	226
40-pDCPD	78	1.19	18.5	282
H-pDCPD	128	0.84	21.3	167
50-pDCPD	109	1.49	22.2	284
H-pDCPD	166	1.15	25.2	176

The morphological characteristics of these aerogels were imaged using SEM, and we found that the fibrillar network characteristic of pDCPD aerogels was conserved after hydrogenation. There were noticeable changes, however, in the hydrogenated aerogel surface areas, pore volumes and pore sizes versus pDCPD analogues (Table 1). On average, H-pDCPD aerogel surface areas decreased by ca. 35 %, pore size increased by ca. 15 % and the pore volume decreased by ca. 20 %.

The oxidative stability of H-pDCPD aerogels was confirmed by thermal treatment of these materials in an oven in air (Figure 4). Samples were heated to 135 °C for 2 hours and the FTIR-ATR spectra were recorded to check for the formation of carbonyl (ca. 1700 cm^{-1}) and/or hydroxyl (ca. 3400 cm^{-1}) absorbances. The pDCPD aerogels heated to this temperature and time underwent discoloration from white to brown/yellow

coincident with formation of strong FTIR absorbances at both 3400 cm^{-1} and 1700 cm^{-1}. In contrast, H-pDCPD aerogels remained nearly white in color (slightly colored, 40- and 50-H-pDCPD due to incomplete hydrogenation) and no new FTIR-ATR absorbances were observed to indicate formation of any oxygen-containing moieties.
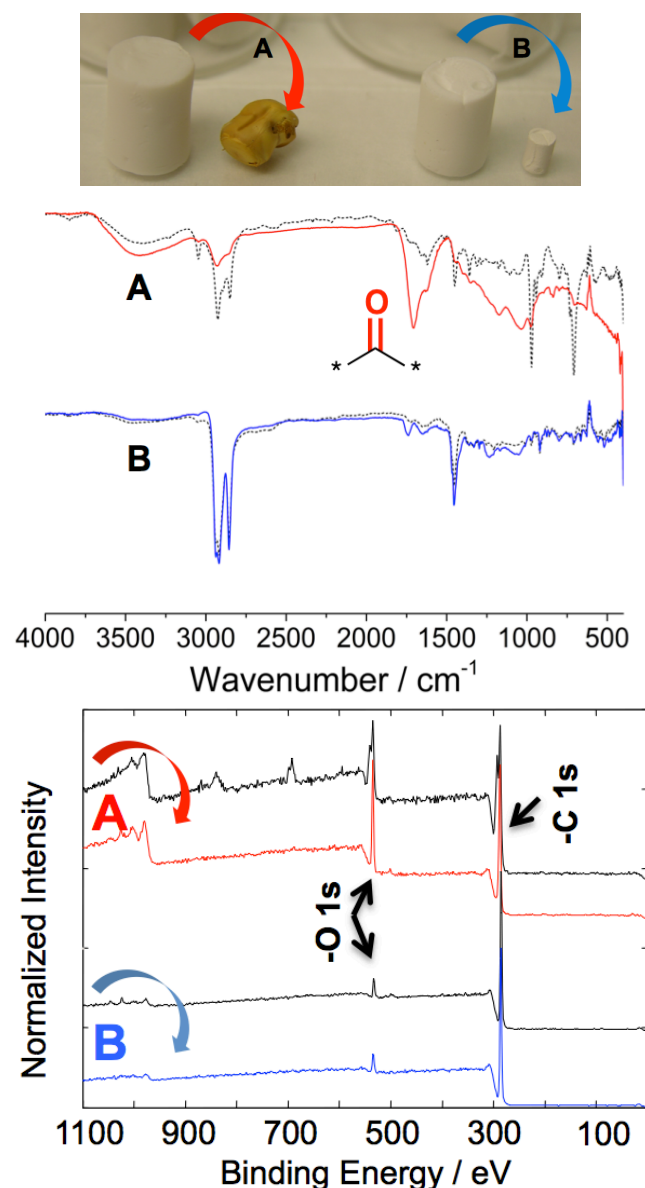

Figure 4. Images (top) of 25-pDCPD (A) and 25-H-pDCPD (B) aerogels before and after thermolysis at 135 °C for 2 hours in air. FTIR-ATR spectra (middle) show formation of carbonyl absorbances at 1700 cm^{-1} for thermalized 25-pDCPD while the spectrum of 25-H-pDCPD remains unchanged. XPS (bottom) spectra before and after thermolysis of aerogels shows an increase in oxygen content for thermalized 25-pDCPD while that of 25-H-pDCPD remains unchanged.

One thermalized sample set was further analyzed using x-ray photoelectron spectroscopy (XPS, Figure 4). The XPS spectrum of 25-pDCPD showed 79.2 % carbon and 16.3 % oxygen with slight contributions from fluorine (4.3 %) and chlorine (<1 %). Thermolysis of this aerogel (135 °C, 2 hours in air) was followed by an increase in the total oxygen content in the

aerogel to 20.5 %. The XPS spectrum of 25-H-*p*DCPD aerogel showed virtually no increase in oxygen content after thermolysis. The hydrogenated aerogel initially consisted of 93.9 % carbon, 4.6 % oxygen and small contributions (ca. 1.5 %) from nitrogen, chloride, sodium and zinc (unknown contaminants). Thermal treatment (135 °C, 2 hours) led to an aerogel composition of 95.3 % carbon and 4.7 % oxygen.
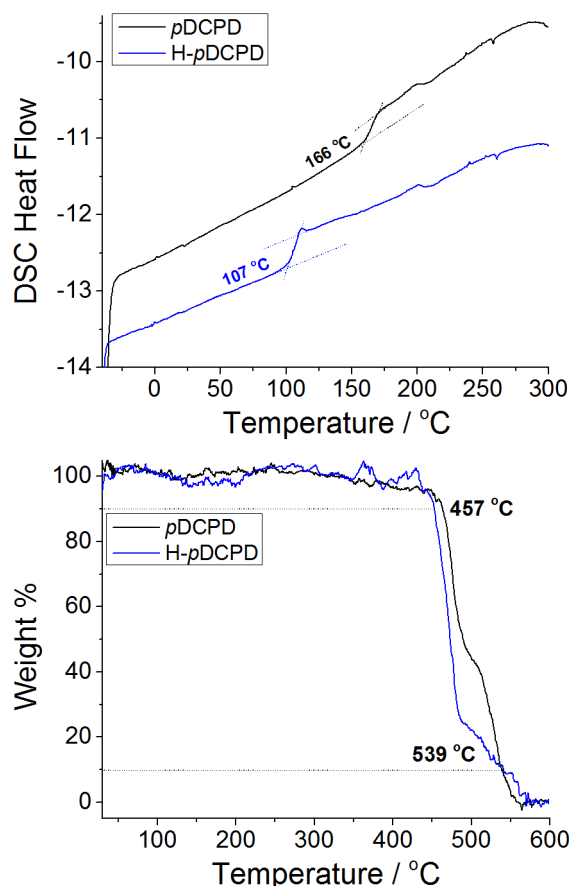

Figure 5. DSC (top) traces of 25-*p*DCPD and 25-H-*p*DCPD aerogels show a reduction in T_g for the hydrogenated aerogel. TGA measurements show both 25-*p*DCPD and 25-H-*p*DCPD do not undergo significant weight loss until ca. 460 °C.

While thermolysis of H-*p*DCPD aerogels confirmed their oxidative stability, one interesting effect was a marked shrinkage of these aerogels as a result of the applied heat. For example, the measured density of 25-H-*p*DCPD was found to be 710 mg mL^{-1} after thermal treatment at 135 °C for 2 hours, a 14-fold increase in aerogel density. By inspection, *p*DCPD aerogels did not suffer such an extreme shrinkage, but the aerogel dimensions became too distorted after heating to reliably calculate a final density in these samples.

The loss in density upon heating is a direct result of the decrease in aerogel T_g upon hydrogenation (Figure 5). Weighing the samples before and after thermolysis shows no change in mass, and TGA measurements (Figure 5) show that both *p*DCPD and H-*p*DCPD aerogels are stable to thermal weight loss to > 400 °C. DSC measurements, on the other hand, show that the T_g of H-*p*DCPD aerogels decreases from 168 ± 4 °C (*p*DCPD) to 111 ± 3 °C.

To probe this effect, 25-*p*DCPD and 25-H-*p*DCPD aerogels were subjected to stepwise thermolysis with density determination after each thermal treatment (Figure 6). Heating these

samples to 80 °C for 16 hours led to slight densification to 40 mg mL^{-1} and 52 mg mL^{-1} respectively and additional heating to 100 °C for 8 hours was followed by additional shrinkage to 46 mg mL^{-1} and 89 mg mL^{-1}. Complete 'shrinkage' of the 25-H-*p*DCPD aerogel was realized after an additional heating to 135 °C for 4.5 hours. Here, the final density of 25-*p*DCPD aerogel was measured as 45 mg mL^{-1} while the density of 25-H-*p*DCPD increased dramatically to 765 mg mL^{-1}. Again, the *p*DCPD aerogel discolored and its FTIR spectrum showed strong absorbances at 3400 cm^{-1} and 1700 cm^{-1} while the H-*p*DCPD aerogel remained white in color and its FTIR spectrum remained virtually unchanged (see SI, Figure S24).
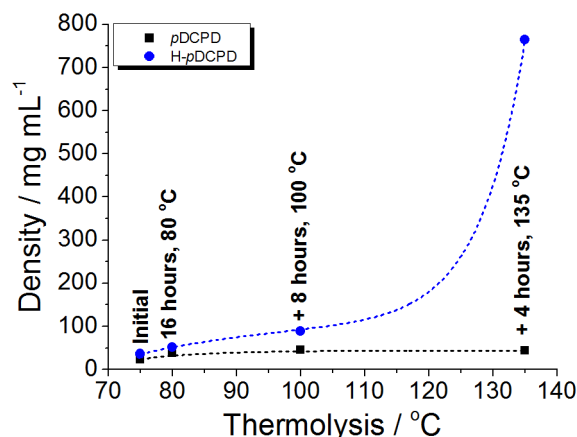

Figure 6. (Top) Evolution of the densities of 25-*p*DCPD and 25-H-*p*DCPD during stepwise thermolysis to a final temperature of 135 °C. 25-H-*p*DCPD shows an abrupt shrinkage when the thermolytic temperature goes above the T_g.

The hydrogenation of *p*DCPD gels to form H-*p*DCPD aerogels therefore significantly increases the oxidative stability of this system while suffering from a decrease in the materials' operating temperature. Characterization of these new aerogels' properties shows that while the fibrillar morphology remains constant, some deviation is observed in the measured pore volume, pore size and aerogel surface area that are consistent with the increase of shrinkage of H-*p*DCPD during aerogel preparation. The inherently low cross-link density of *p*DCPD aerogels may be responsible for the observance of T_gs in these materials at 168 °C (*p*DCPD) and 111 °C (H-*p*DCPD) and the ability of these materials to shrink at temperatures above T_g. The ease of preparation of these H-*p*DCPD aerogels and their increased oxidative stability creates the need for synthesizing *p*DCPD gels of increasing cross-link density prior to hydrogenation. We believe these materials may be less susceptible to shrinkage during supercritical drying and may increase the operating temperature for the hydrogenated system.

ASSOCIATED CONTENT

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Author Contributions

All authors have given approval to the final version of the manuscript.

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Table of Contents Artwork:

Hydrogenation = Oxidative Stability

4*H